Characterization of Thermoreversible Gels Composed of Monodisperse Rodlike Particles: Rheology and Scattering

Naveen Krishna Reddy[1], *Zhenkun Zhang*[1], *Pavlik Lettinga*[2], *Jan Dhont*[2] *and Jan Vermant*[1]

[1]*Department of Chemical Engineering, K.U.Leuven, W. de Croylaan 46, B-3001 Leuven, Belgium*
[2] *Research Centre Jülich, Institute of Solid State Research, Soft Condensed Matter, Jülich, Germany*

Introduction

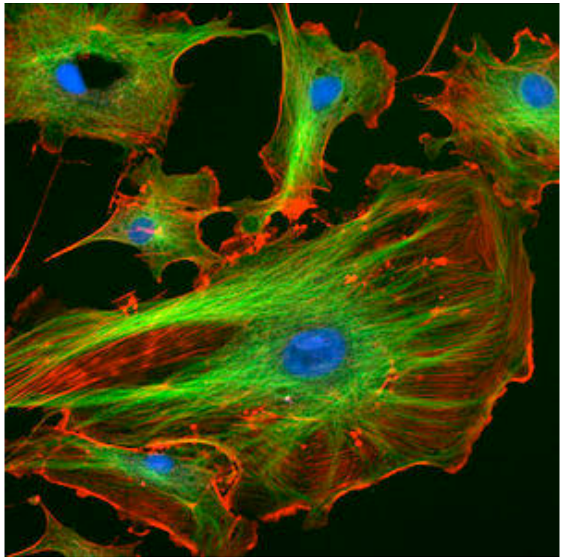
Gels, under flow are liquid,
but behave like solid at rest

Paint

Properties

- high moduli
- yield stress
- long relaxation times
- shear thinning
- thixotropy

Food



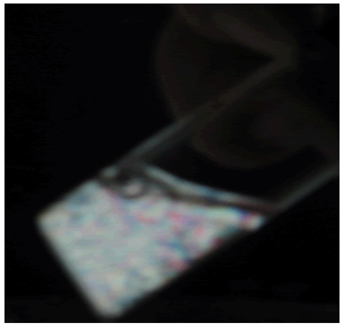
Eukaryotic cytoskeleton

http://en.wikipedia.org/wiki/

Introduction

Advantages of gels composed of rod-like particles

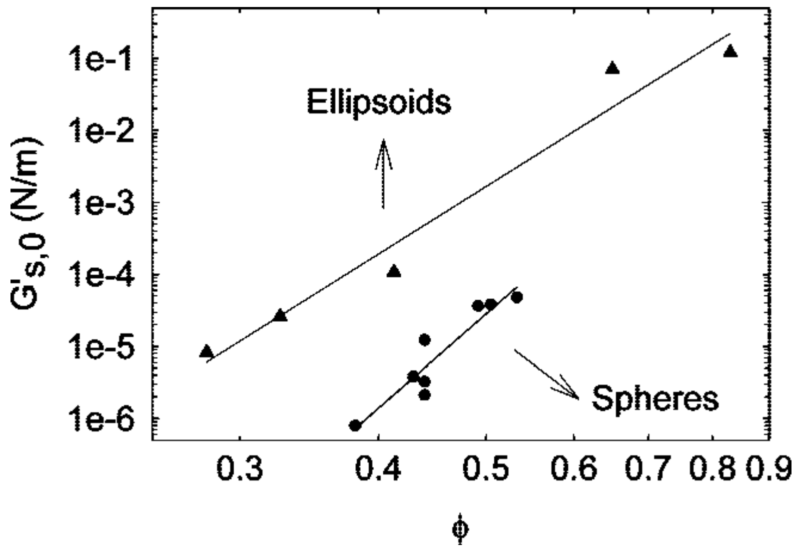
- Relatively low volume fraction needed to form a gel
- Different phases (isotropic, nematic, smectic, columnar)
- Higher gel strength (compared to that made of spheres)
- Relevant to biological cells (actin, protein filaments)



Nematic fluid

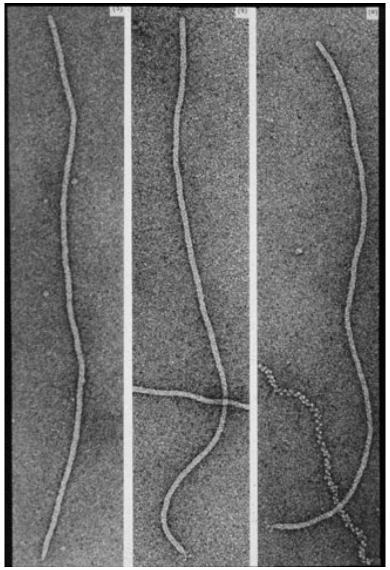
Nematic gel

Zhang *et al.* Langmuir, 2009, 25 (4), pp 2437

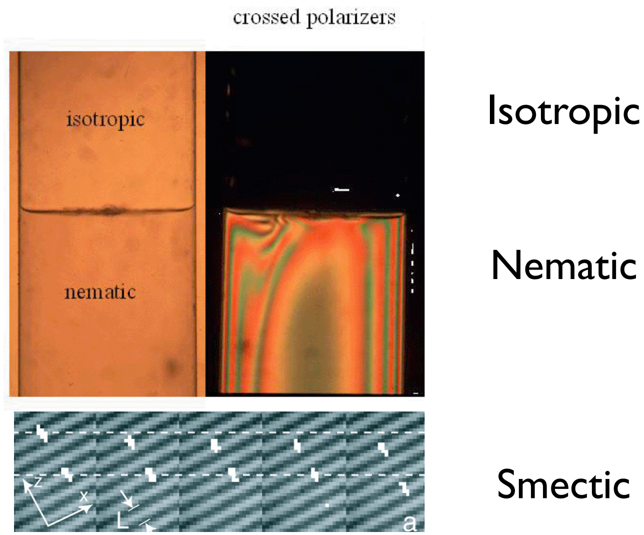


Basavaraj *et al.* Langmuir, 2009, 25 (5), pp 2718–2728

Introduction



fd-virus



- Mono-disperse (*Length=880 nm, dia.=6.6 nm, P_L=2200 nm*)
- Negatively charged (*10 e^-/nm at 8.2 pH*)
- Surface groups (*-COOH, -OH, -NH_2*)

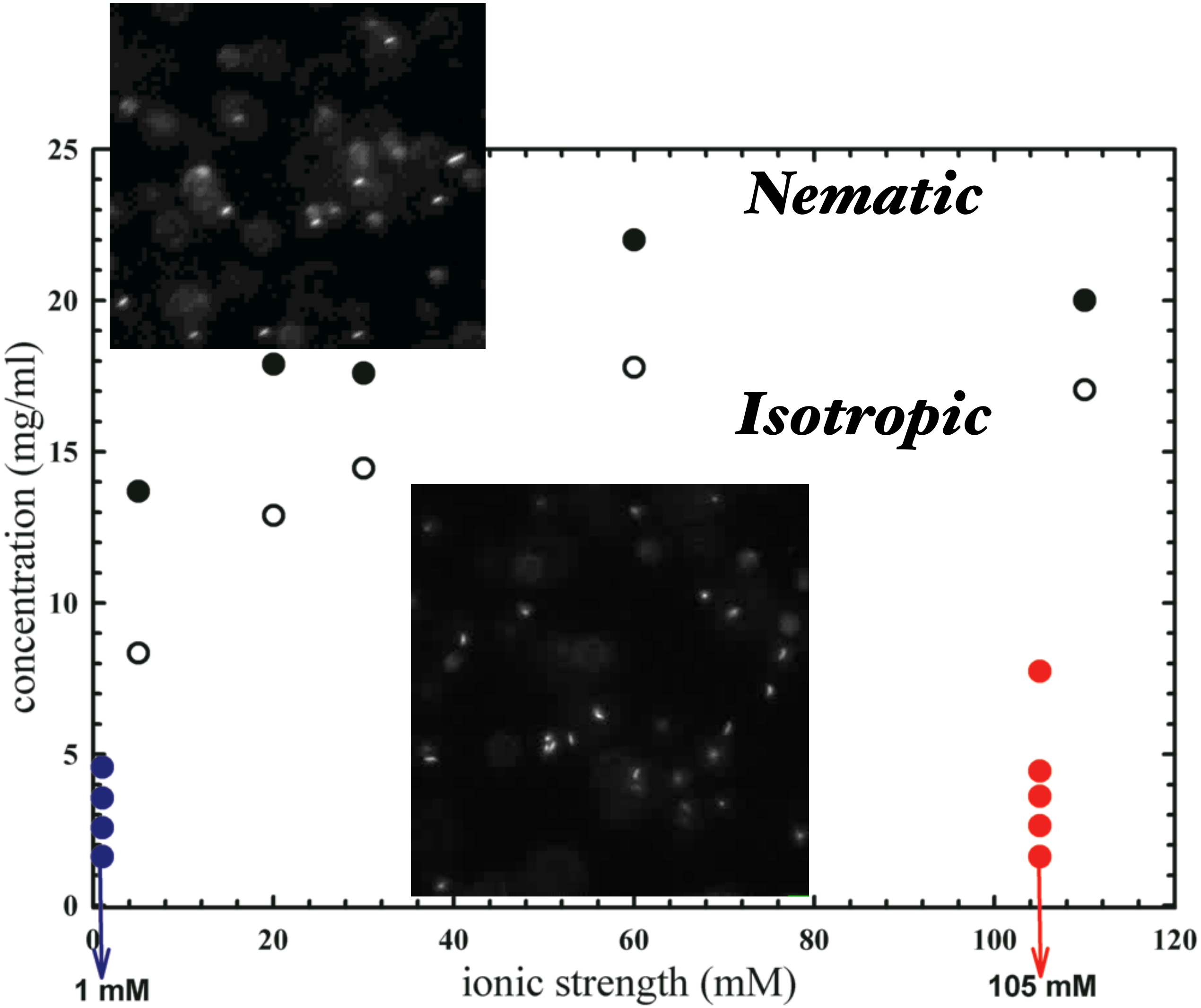
www.elsie.brandeis.edu/.../FD_Virus.htm
http://www.rowland.harvard.edu/rjf/dogic/fdvirus.php

M. Paul Lettinga and Eric Grelet Phys. Rev. Lett. 99, 197802 (2007)

Outline

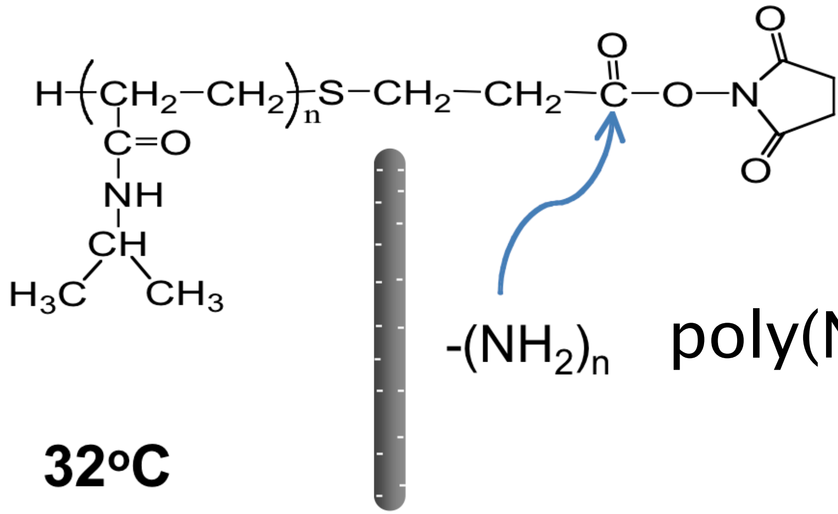
1. Introduction
2. Phase diagram and gel structure
3. Results
   - Gel point
   - Rheology
   - Scattering
4. Conclusions

Phase diagram solution

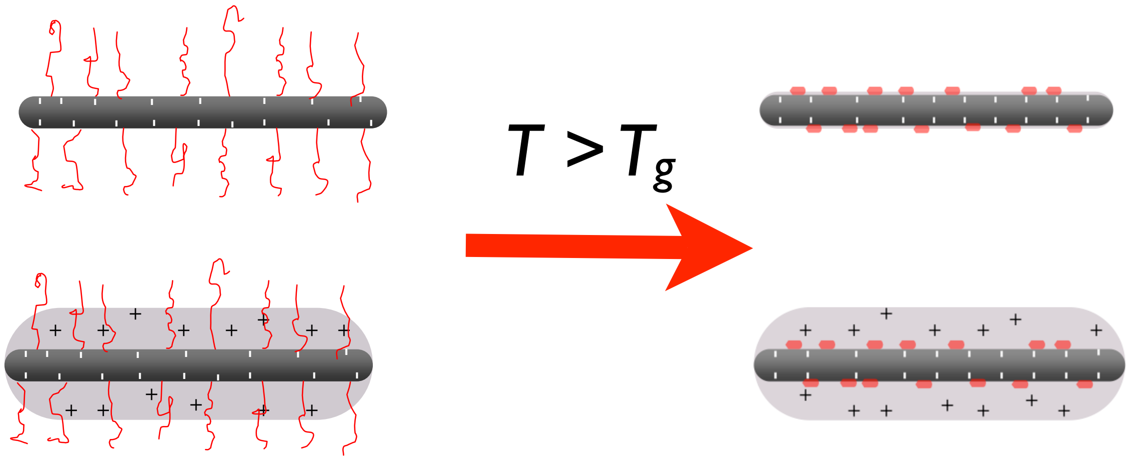


Zhang *et al.* Langmuir, 2009, 25 (4), pp 2437

Gelation



poly(N-isopropylacrylamide)



10 nm

$$D_{eff}^{Polymer} = D_{fd} + 4R_g$$

$$D_{eff}^{electrostatic} = D_{fd} + f(k^{-1})$$

26 nm

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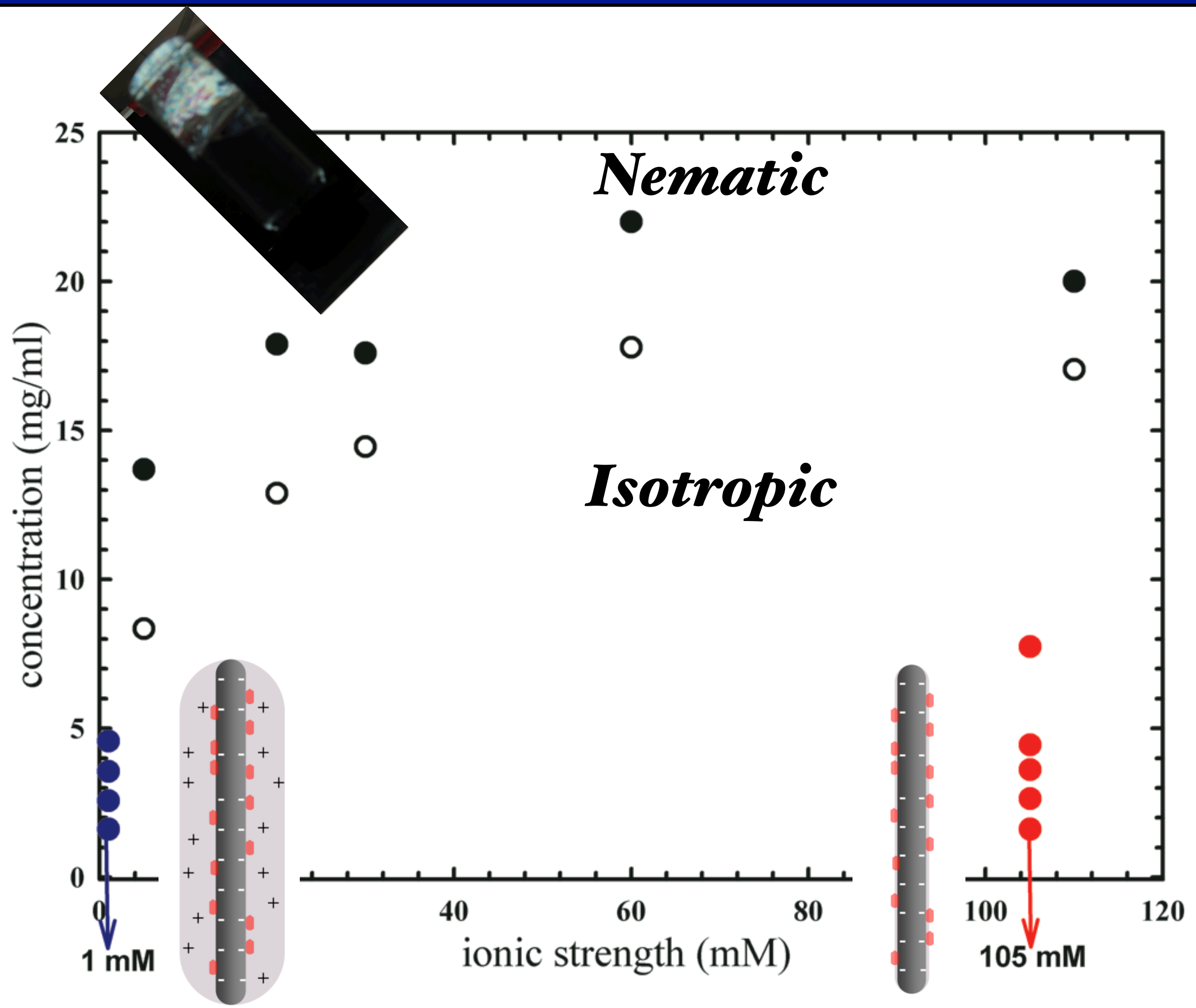
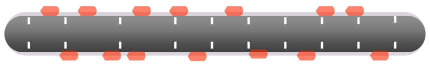
Phase diagram gel



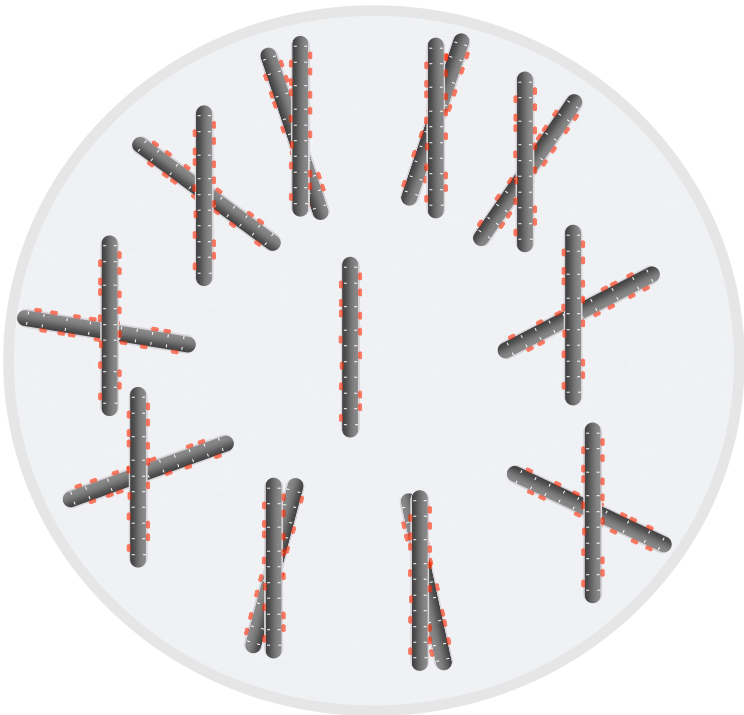
Zhang *et al.* Langmuir, 2009, 25 (4), 2437

Possible gel structure

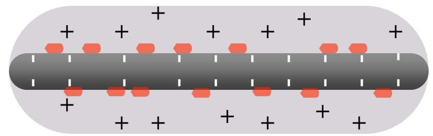
105 mM



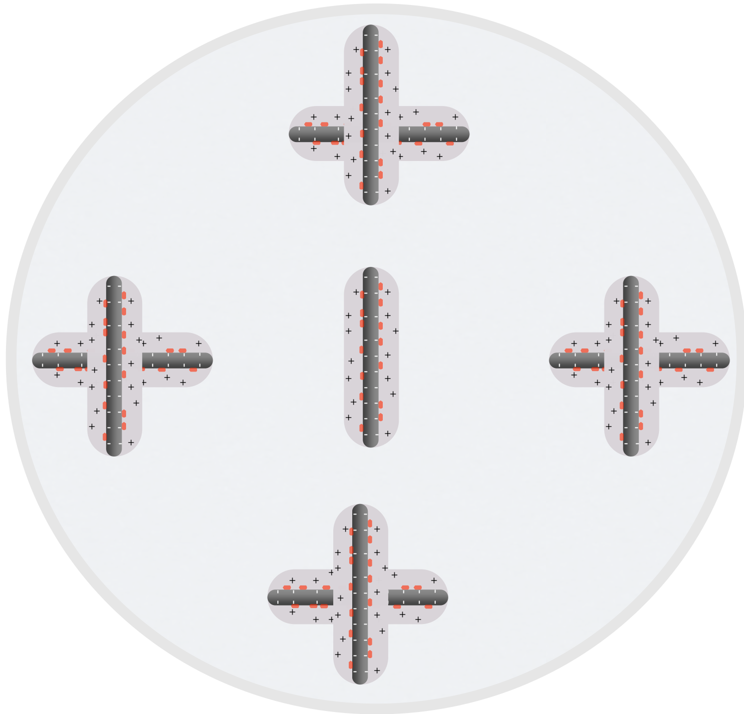
Diffusion



1 mM



Diffusion + *barrier*



Outline

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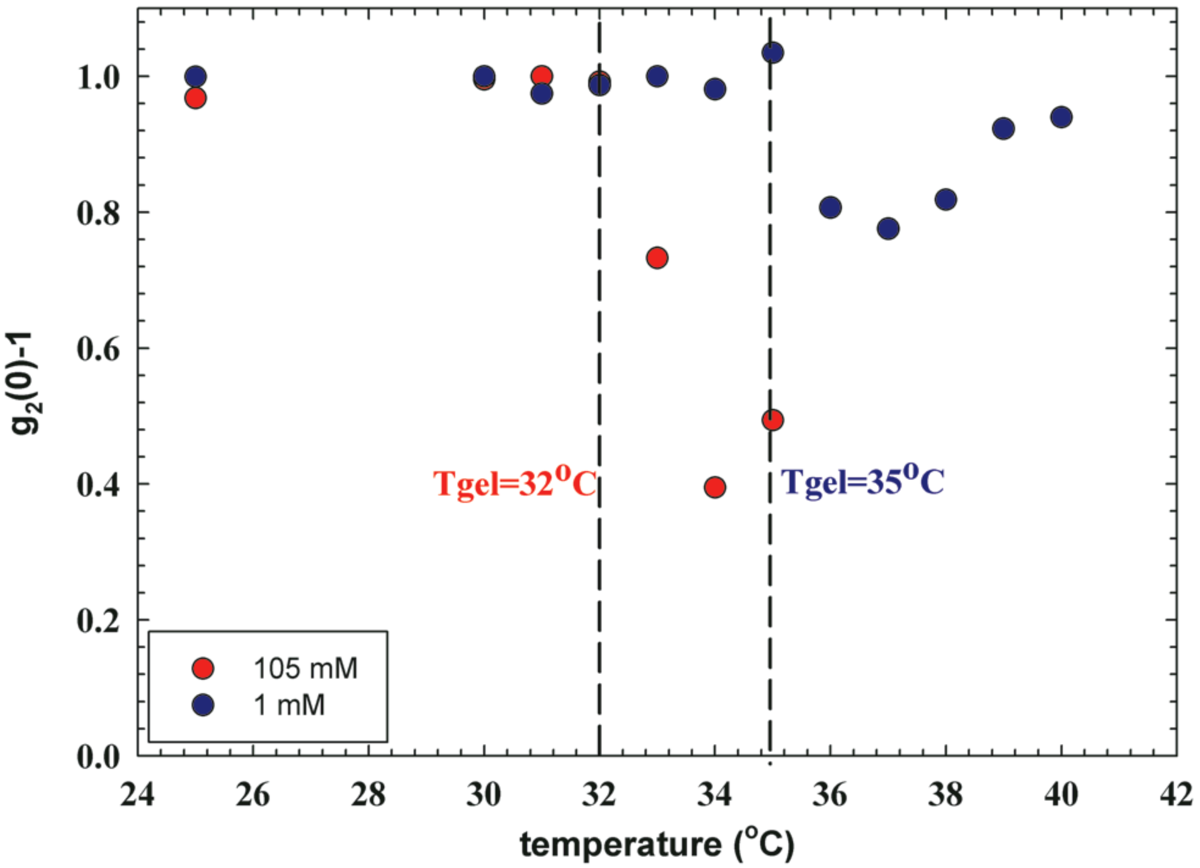
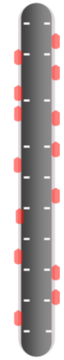
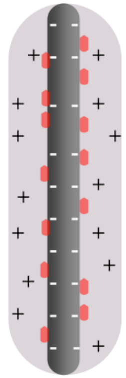
3. Results
   - Gel point: *Dynamic light scattering*
   - Rheology
   - Scattering
4. Conclusions

Gel point: Dynamic light scattering







Shift in gelation temperature due to electrostatic double layer

Outline

1. Introduction
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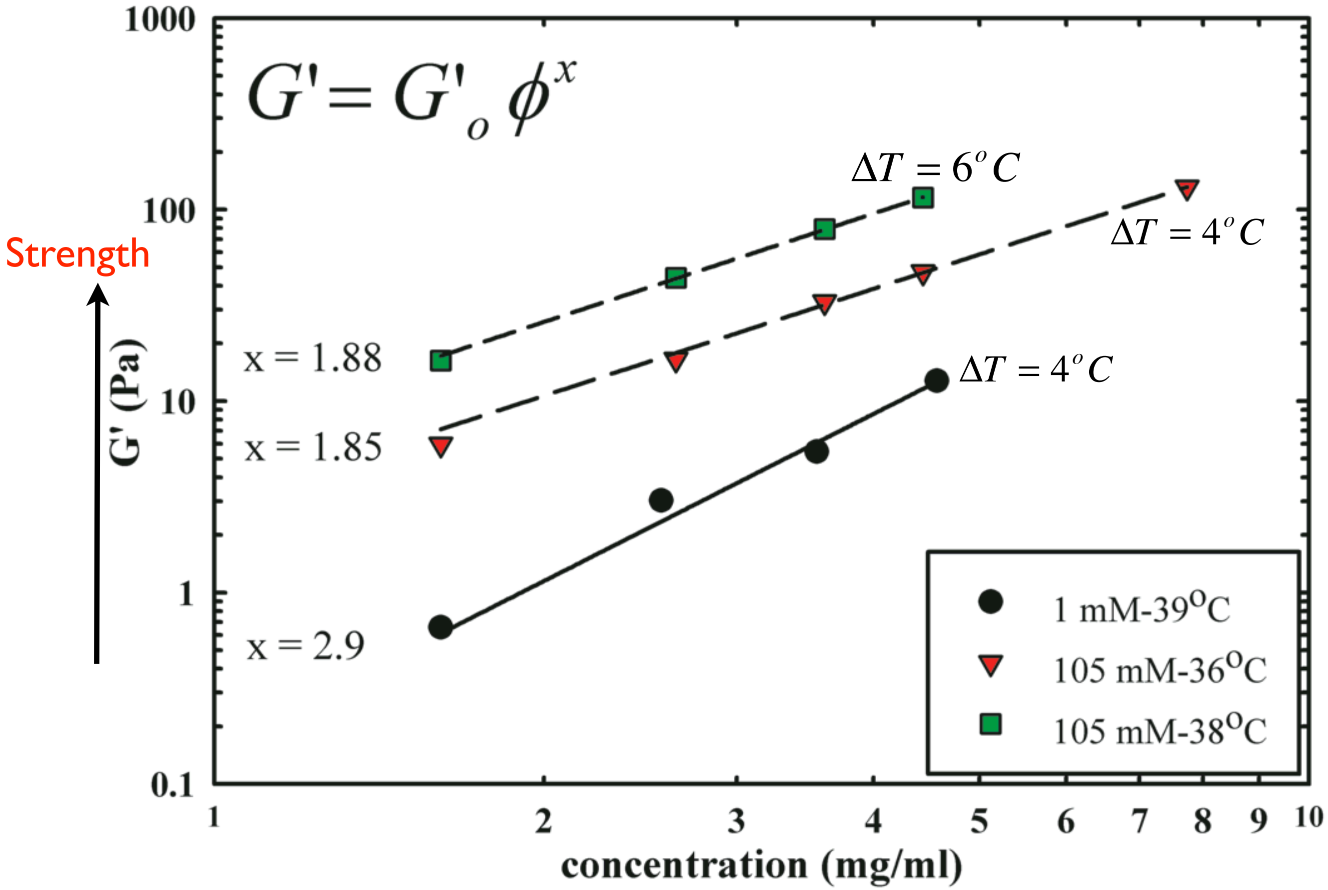
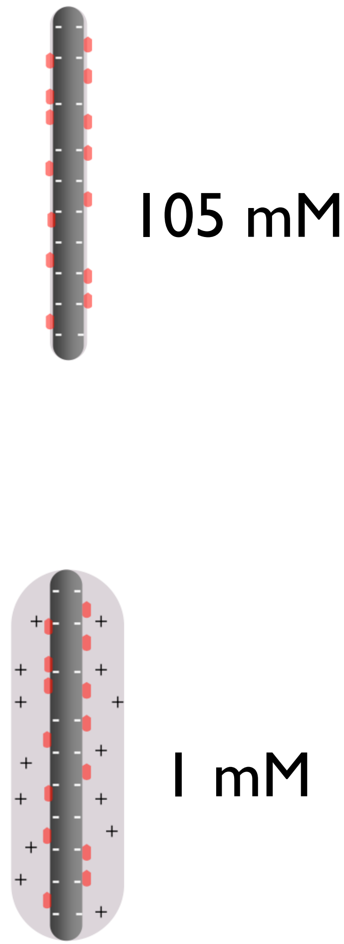
3. Results
   - Gel point
   - Rheology
     - Linear Viscoelasticity
       - *Strength and structure*
     - Yield stress
   - Scattering
4. Conclusions

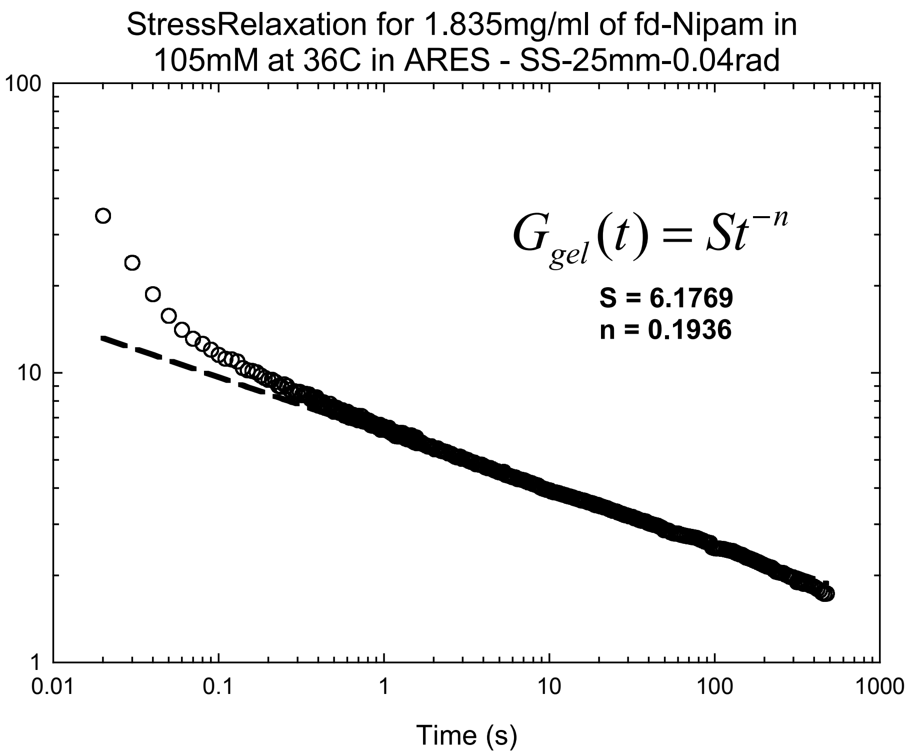
Storage modulus





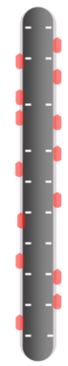
Characteristic length or structure changes with ionic strength but not with temperature

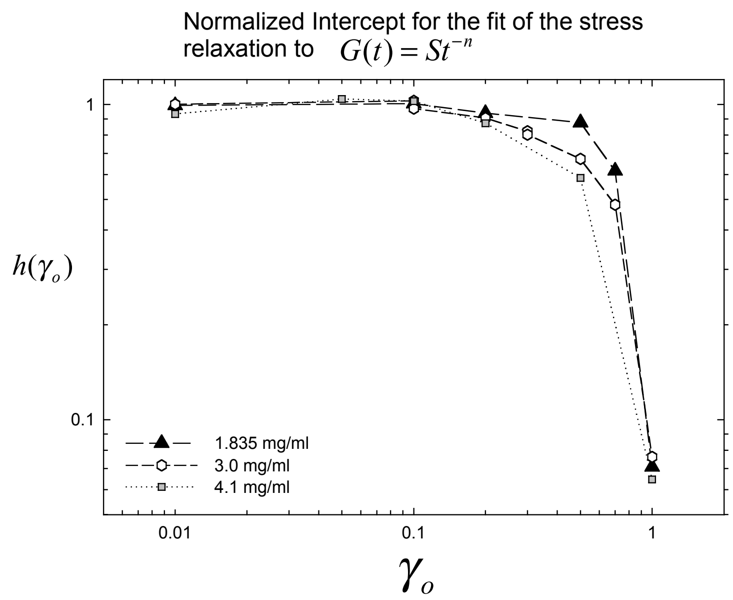
Stress Relaxation



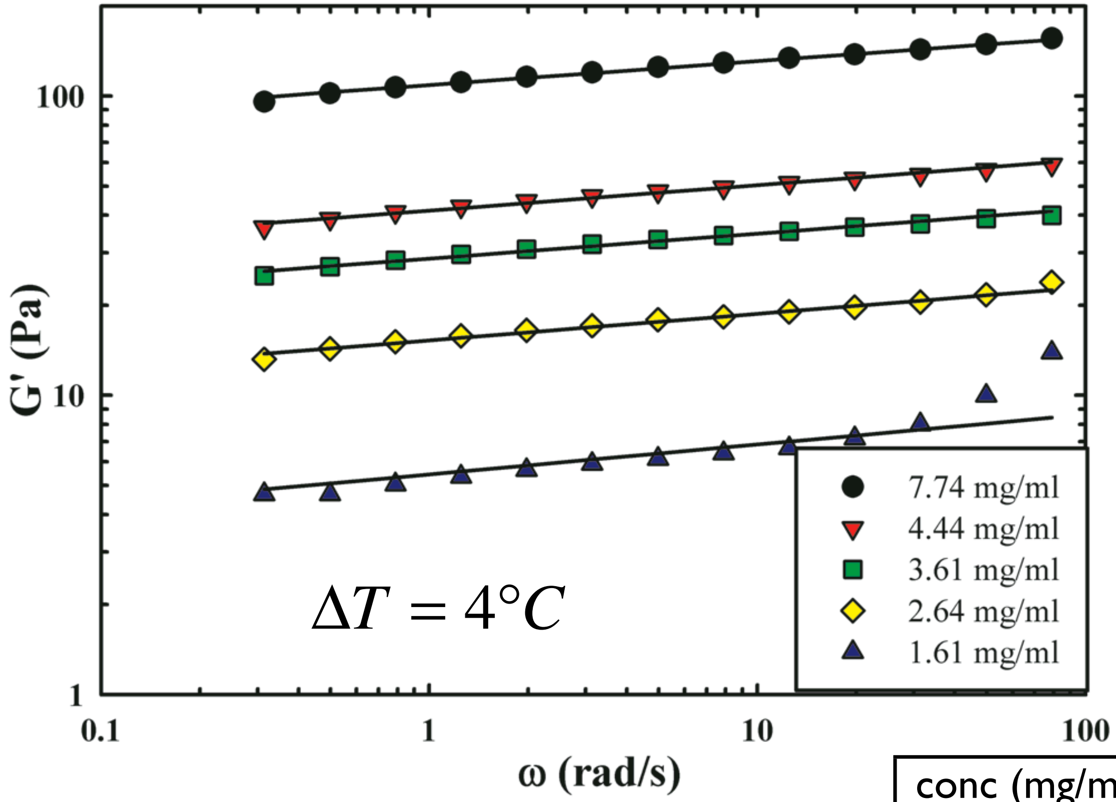
conc. (mg/ml) 105 mM	G'	
	S	n
1,61	7,05	0,149
2,64	18,9	0,15
3,61	36,0	0,15

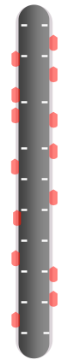
105 mM





Frequency sweep





105 mM

Critical gel

$$G(t) = St^{-n}$$

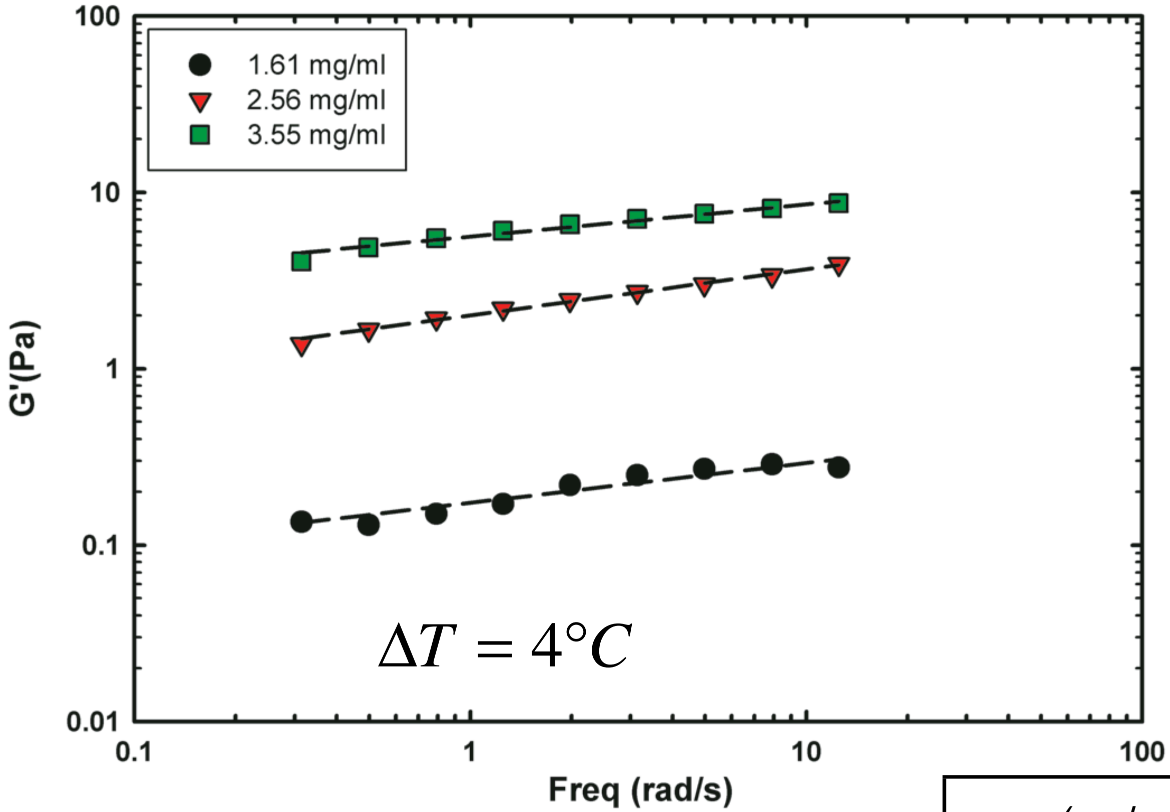
Strength Structure

conc (mg/ml) 105 mM	G'	
	S +/- 0.5	n +/- 0.002
1,61	7,0	0,12
2,64	17,0	0,12
3,61	32,0	0,12
4,44	46,0	0,12
7,74	120,0	0,12

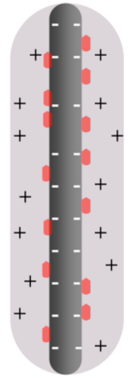
$$G'_{gel}(\omega) = \Gamma(1-n)\cos\left(\frac{n\pi}{2}\right)S\omega^{n}$$

Winter et al., JOR. 30, 367 (1986)

Frequency sweep



$$\Delta T = 4°C$$



1 mM

Critical gel

$$G(t) = S t^{-n}$$

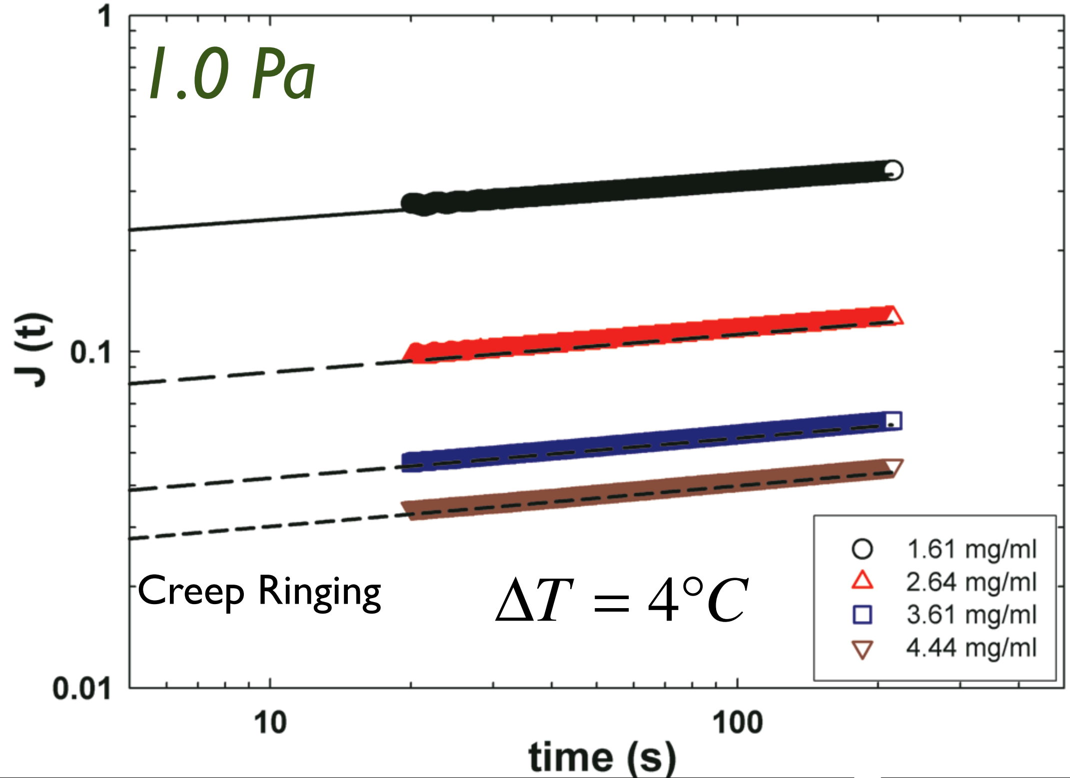
Strength Structure

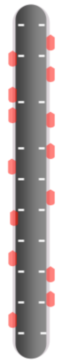
conc (mg/ml) 1 mM	G'	
	S +/- 0.05	n +/- 0.04
1,61	0,15	0,22
2,54	1,7	0,22
3,55	5,0	0,22

$$G'_{gel}(\omega) = \Gamma(1-n)\cos\left(\frac{n\pi}{2}\right) S \omega^{n}$$

Winter et al., JOR. 30, 367 (1986)

Creep





105 mM

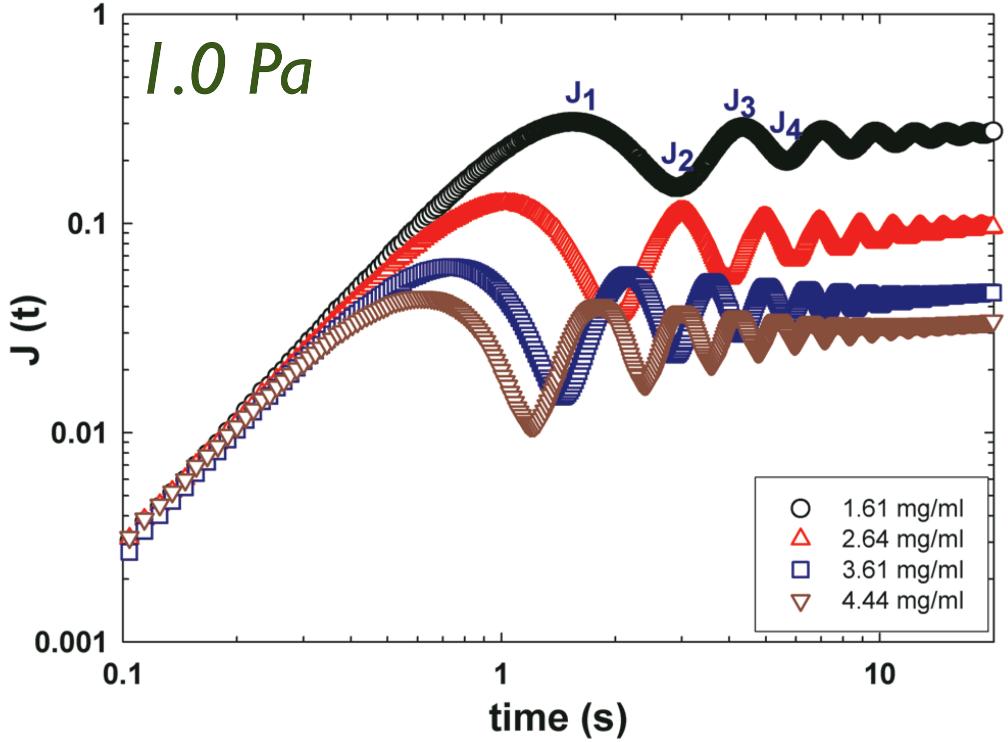
$$J(t) = \frac{t^n}{S\Gamma(1-n)\Gamma(1+n)}$$

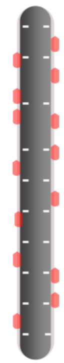
Venkataraman et al. Rheol. Acta, 29, 423 (1990)

conc (mg/ml) 105 mM	Oscillatory	
	S +/- 0.5	n +/- 0.02
1,61	7	0,12
2,64	17	0,12
3,61	32	0,12
4,44	46	0,12

conc (mg/ml) 105 mM	Creep	
	S +/- 0.5	n +/- 0.02
1,61	5	0,14
2,64	14	0,14
3,61	30	0,14
4,44	40	0,14

Creep Ringing





105 mM

$$\tan(\delta) \approx \frac{\Delta}{\pi}$$

$$\Delta = 2\ln\left(\frac{J_1 - 2J_2 + J_3}{-J_2 + 2J_3 - J_4}\right)$$

$$G' \approx \frac{I\omega^2}{b}[1 + (\Delta/2\pi)^2]$$

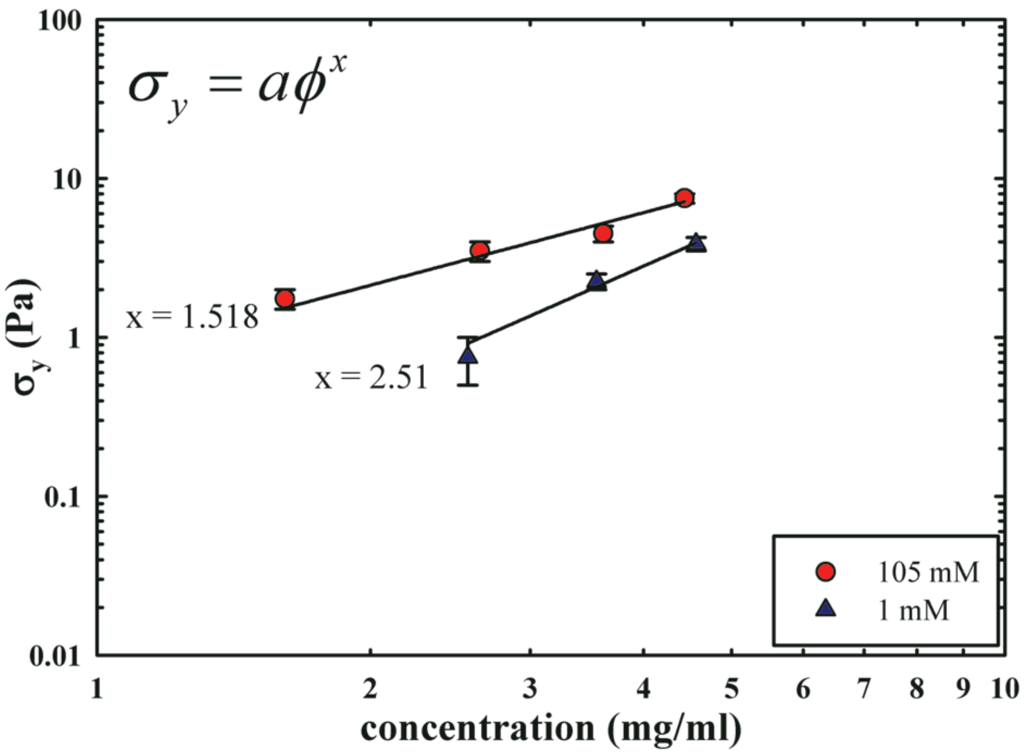
$$G'' \approx \frac{I\omega^2}{b}(\Delta/\pi)$$

$$b_{c-p} = \frac{2\pi r^3}{3\tan(\theta)}$$

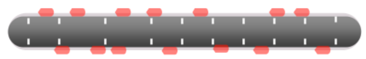
Conc. (mg/ml)	Freq. (rad/s)	Creep Ringing		Forced Oscillations	
		G' (Pa)	G'' (Pa)	G' (Pa)	G'' (Pa)
1,61	2,0	6,9	0,55	5,6	0,62
2,64	3,2	17	1,06	17	1,8
3,61	4,4	32,2	1,75	32,8	3,5
4,44	5,3	47	2,25	49,5	5,35

Ewoldt et al. Rheol. Bull. 76, 4 (2007)

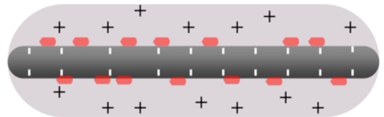
Yield stress



105 mM



1 mM



$$x = \frac{d-1}{d-D_f}$$

	D_f (rheology)	
[I]	σ_y	G', γ_c
105 mM	1,7	1,7
1 mM	2,2	2,05

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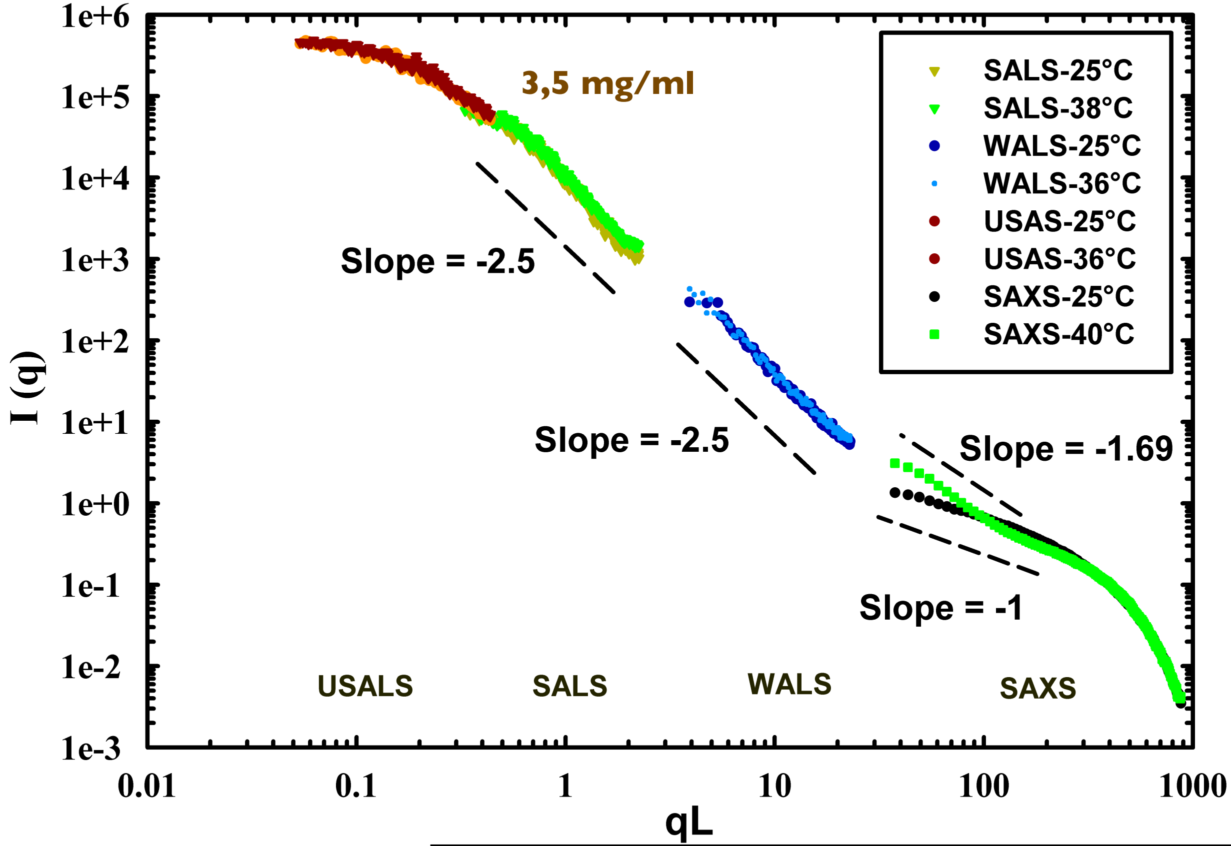
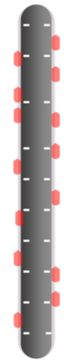
Scattering 105 mM



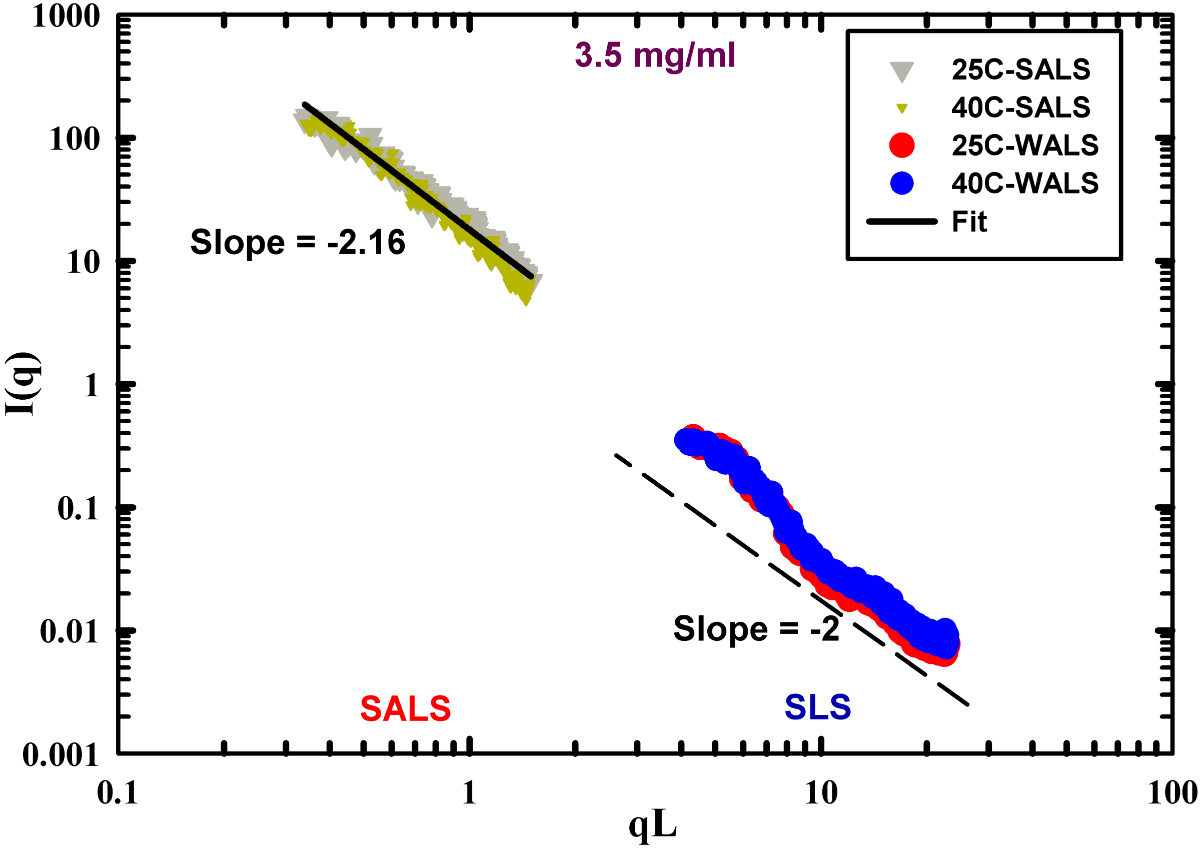
105 mM



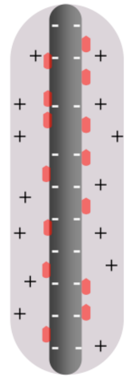
	D_f		
[I]	σ_y	G', γ_c	Scattering
105 mM	1,7	1,7	1,69*
1 mM	2,2	2,05	

* low q in SAXS

Scattering 1 mM



1mM



	D_f		
[I]	σ_y	G', γ_c	Scattering
105 mM	**1,7**	**1,7**	**1,69***
1 mM	**2,2**	**2,05**	**2,16**

* low q in SAXS

Conclusion

1. **Gel structure and T_{gel}**
   - *ionic strength*
2. **Linear viscoelastic limit**
   - *power law scaling - critical gel*
   - *unique **S**(conc. and [I]) and **n**([I])*
3. **Fractal dimension - yield stress and G' & γ_c**
   - *1,7 for gels in 105 mM [I] (DLCA)*
   - *2,2 for gels in 1 mM[I] (RLCA)*
4. **Fractal dimension - scattering technique**
   - *1,7 for gels in 105 mM [I] (DLCA) - only at low q regime SAXS*
   - *2,2 for gels in 1 mM[I] (RLCA)*

NANODIRECT

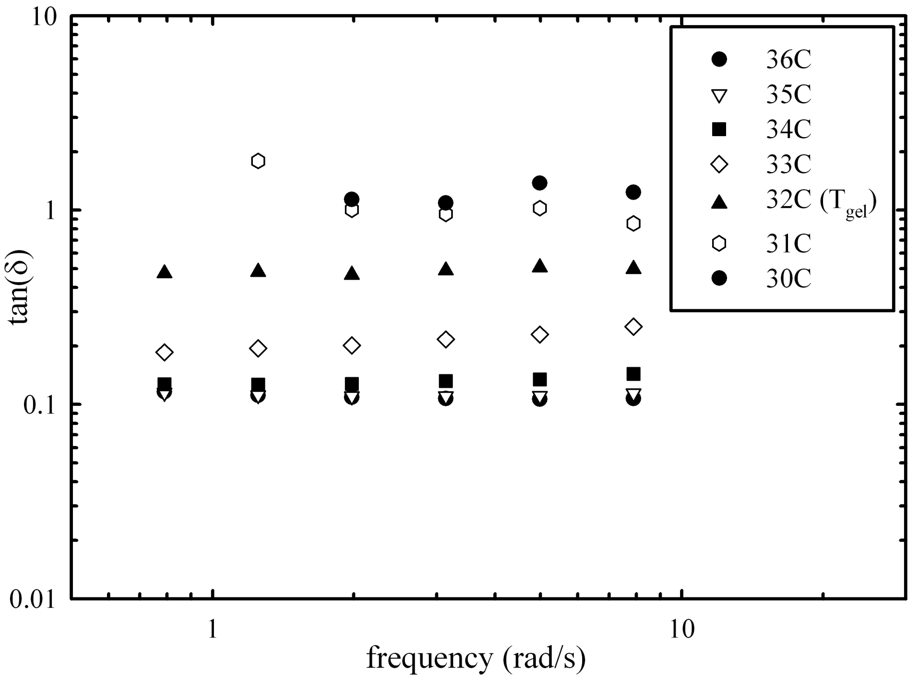
Thank you

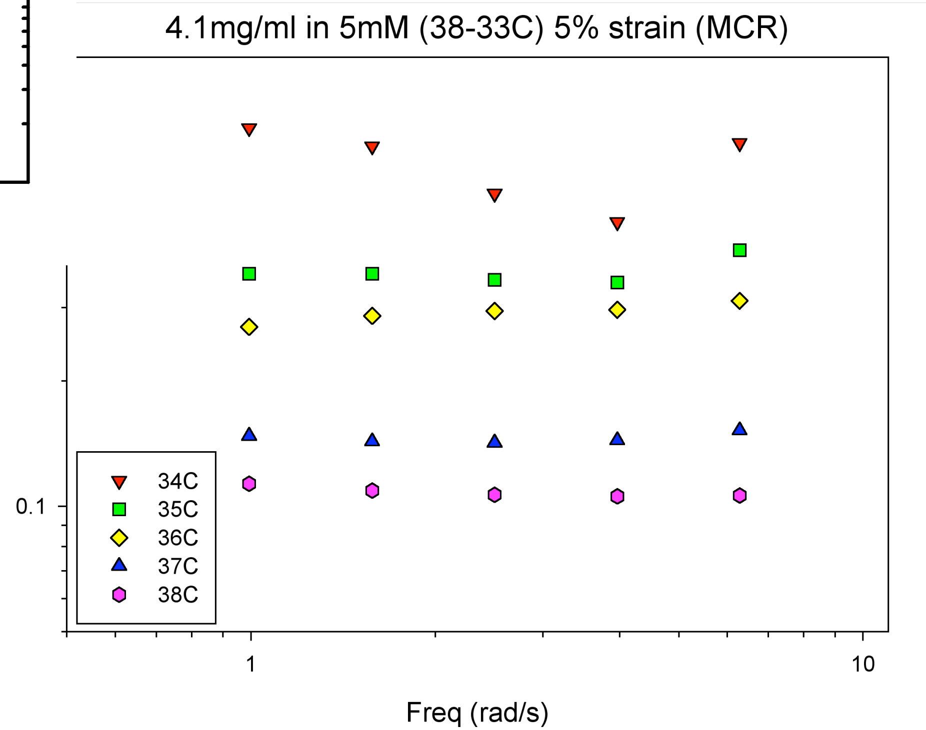
No. grafted Polymer

Number of PNIPAM polymers per virus Since the refractive index increment (*dn*/*dc*) is proportional to the mass density, the *dn*/*dc* difference between the bare virus and the PNIPAM-*fd* is due to the grafted polymer. This can be used to estimate the number of grafted polymers on each virus.10 The *dn*/*dc* of carboxyl-terminated PNIPAM ((*dn*/*dc*)p) and *fd* virus ((*dn*/*dc*)*fd*) were determined with the homemade scanning Michelson differential interferometer at T = 25°C 6. As for PNIPAM-*fd* system, the concentration of *fd* virus in PNIPAM-*fd* suspensions can be easily obtained by UV absorption (PNIPAM does not absorb in the UV range where *fd* absorbs). So an apparent *dn*/*dc* can also be determined based on the virus concentration ((*dn*/*dc*)app). The number of PNIPAM grafted on each virus, *N*, can be estimated by the following equation1

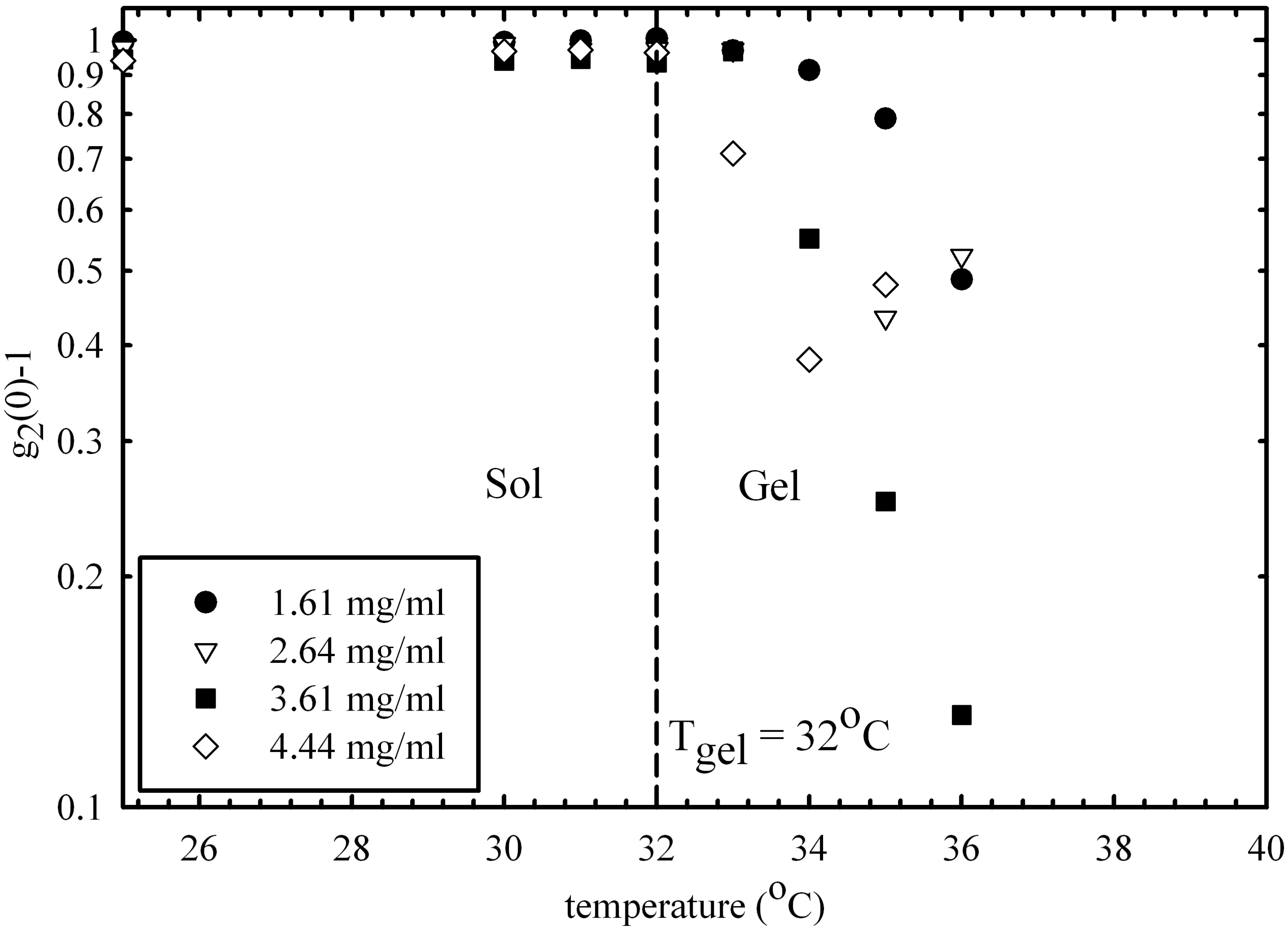
$$\mathrm{Vol}_{\mathrm{eff}} = C_{fd}\, N_A\, L\, pi\, (D_{eff} / 2)^2 / M_w$$

Gel temperature from Rheology



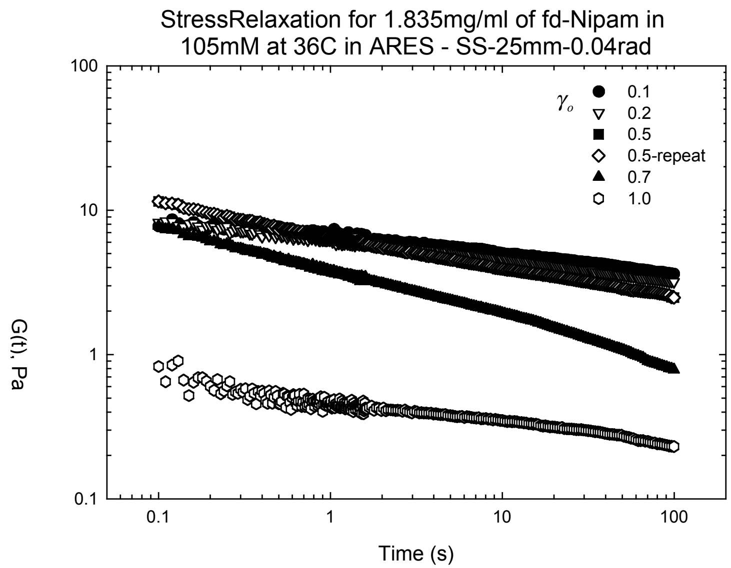


DLS

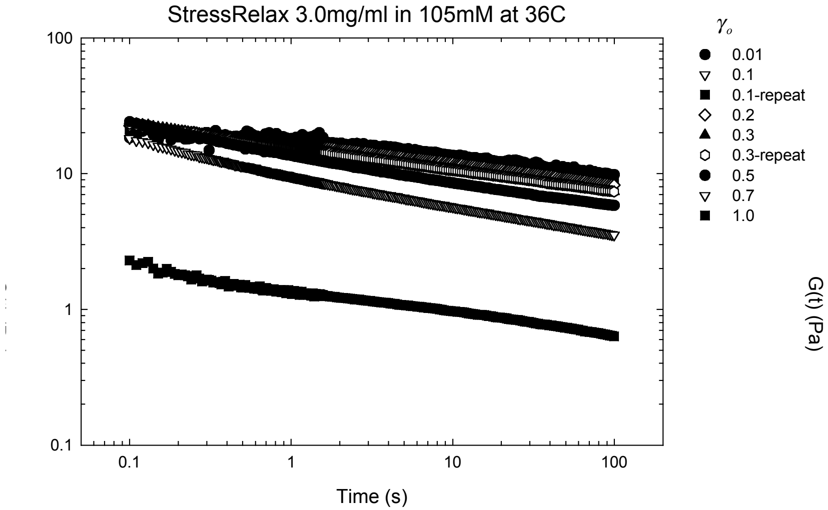


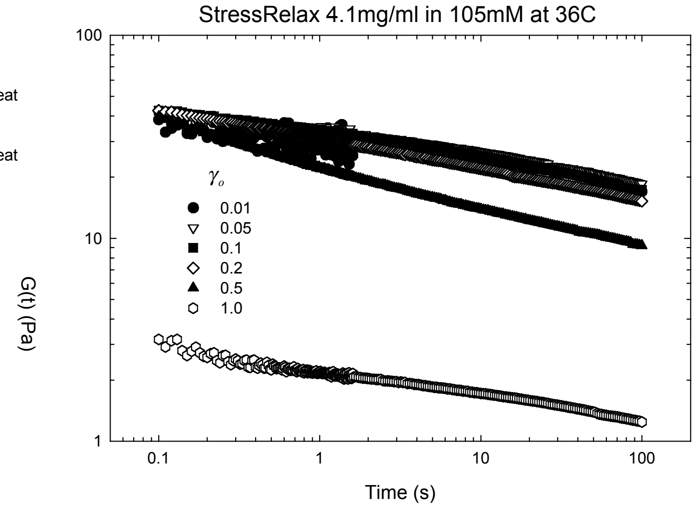
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$g_2(0)$-1
26
28
30
32
34
36
38
40
temperature (^oC)
Sol
Gel
$T_{gel} = 32^oC$
1.61 mg/ml
2.64 mg/ml
3.61 mg/ml
4.44 mg/ml

Stress Relaxation

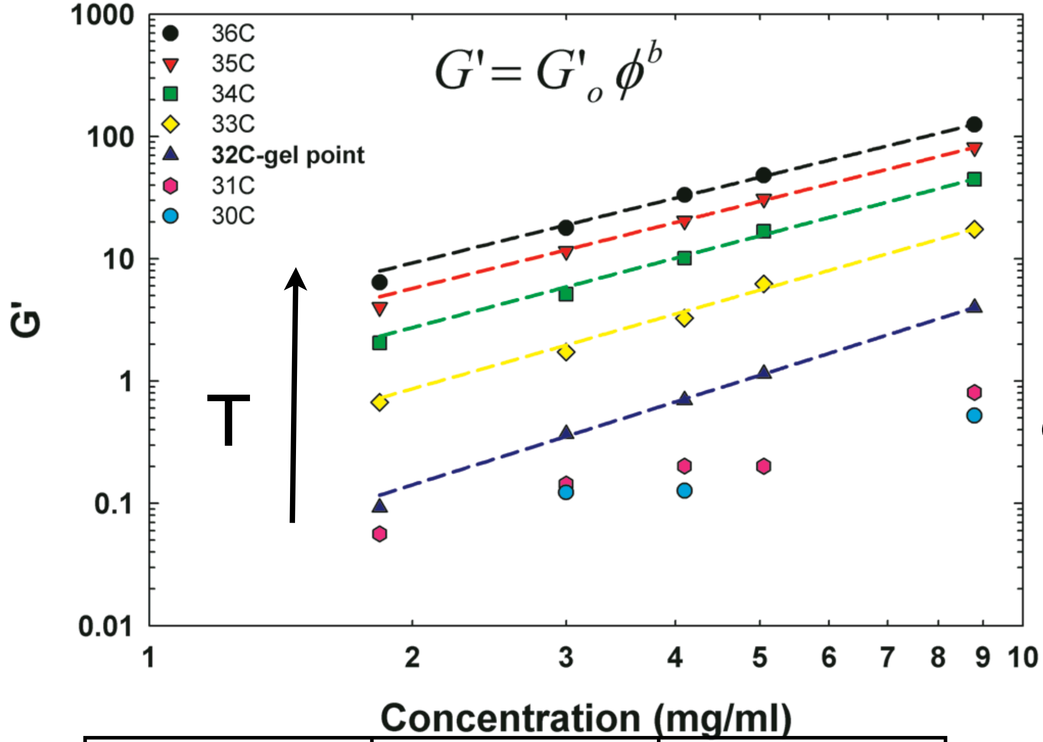


The yielding (nonlinear regime) strain decreases with the conc. (Meaning that the system become more brittle with inc. in conc.). Also can be seen in strain sweep (indicating brittle)





Percolation theory scaling



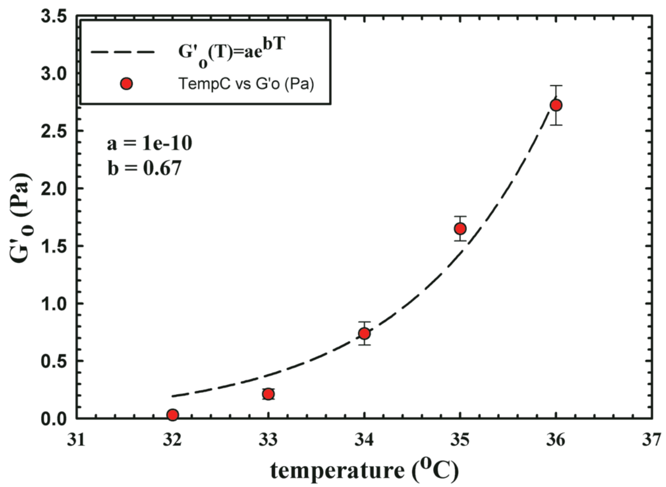
$$G' = G_o(\phi - \phi_g)^b$$ *Grant and Russel*

$$G' = G_o\left(\frac{\phi}{\phi_g} - 1\right)^b$$ *Zukoski et al.*

$$G' = \frac{G_o}{\phi_g^{\,b}}(\phi - \phi_g)^b = G_o(T)(\phi - \phi_g)^b$$

Bergstrom et al.

Temp	G'o(Pa)	b
36	2,72	1,76
35	1,65	1,79
34	0,74	1,88
33	0,21	2,03
32	0,03	2,25

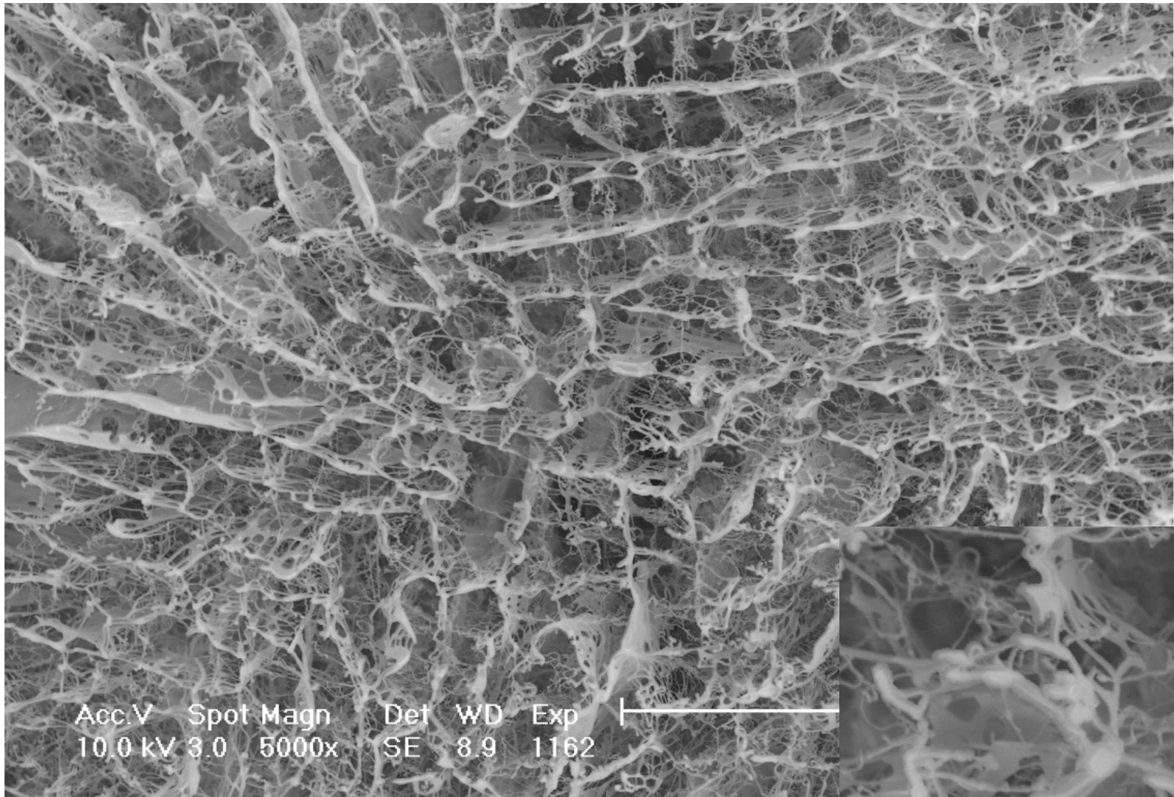


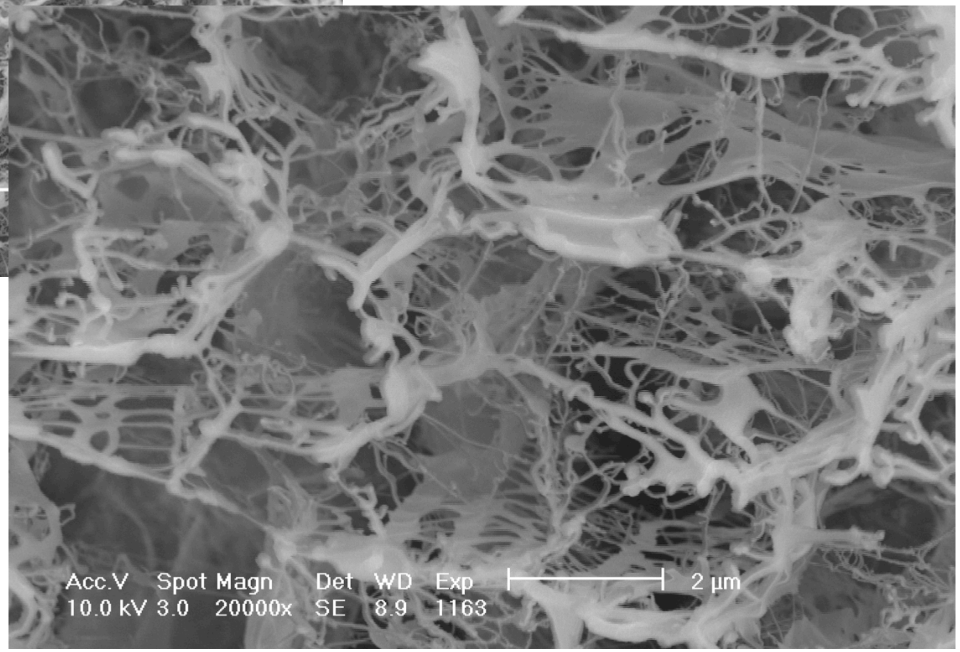
M. C. Grant and W. B. Russel, Phys. Rev. E 47, 2606 - 2614 (1993)

C. J. Rueb and C. F. ZukoskiJ. Rheol.Volume 41, Issue 2, pp. 197-218 (March 1997)

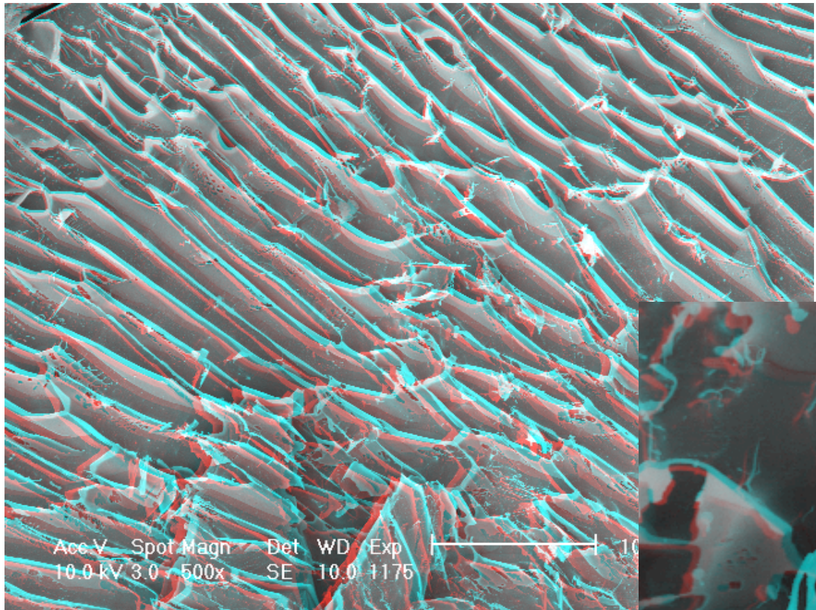
Yanez *et al.* J. Coll. Interf. Sci., 209, 162 (1999)

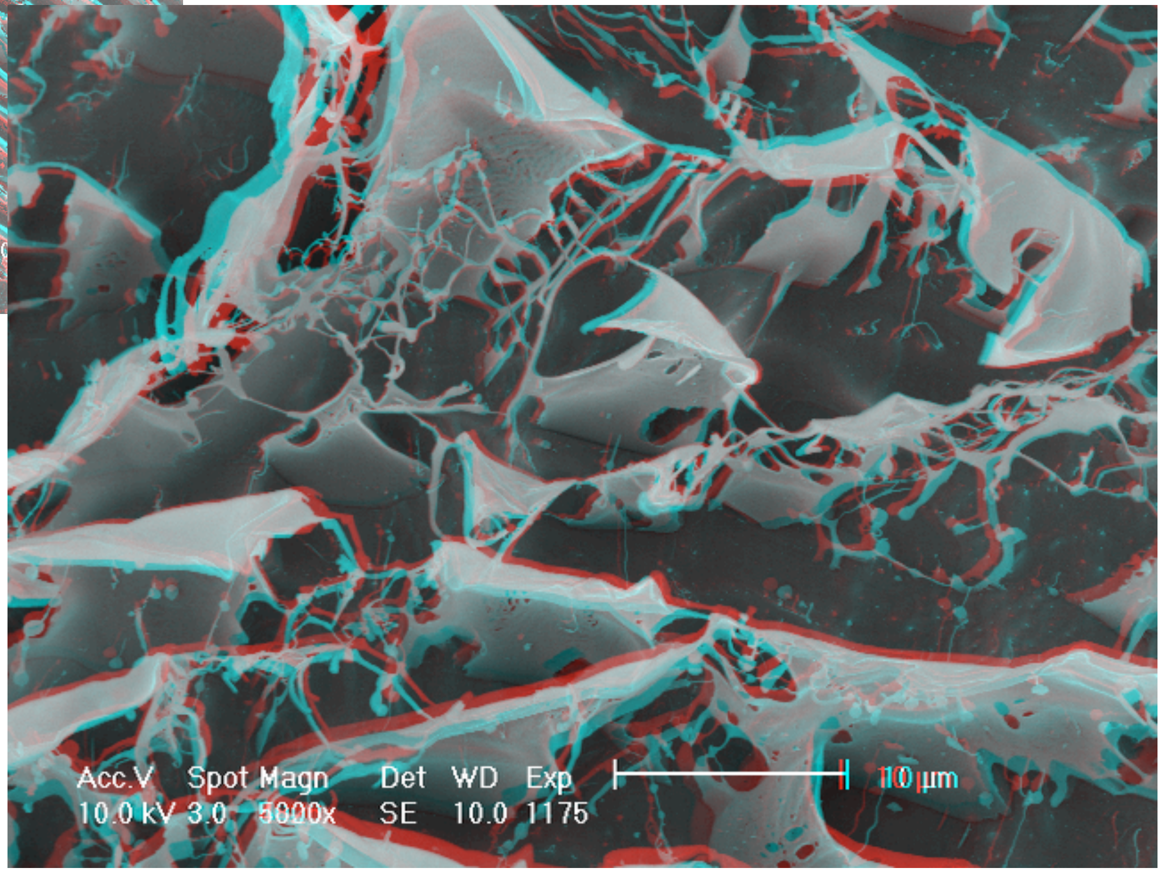
Cryo SEM (1 mM) Liquid



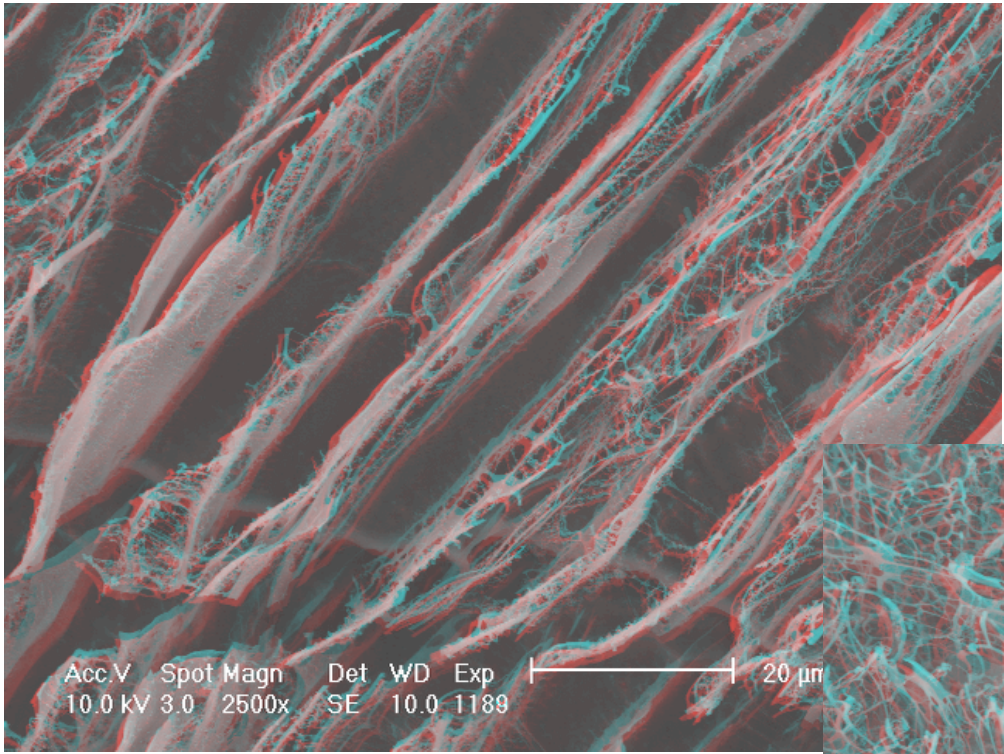


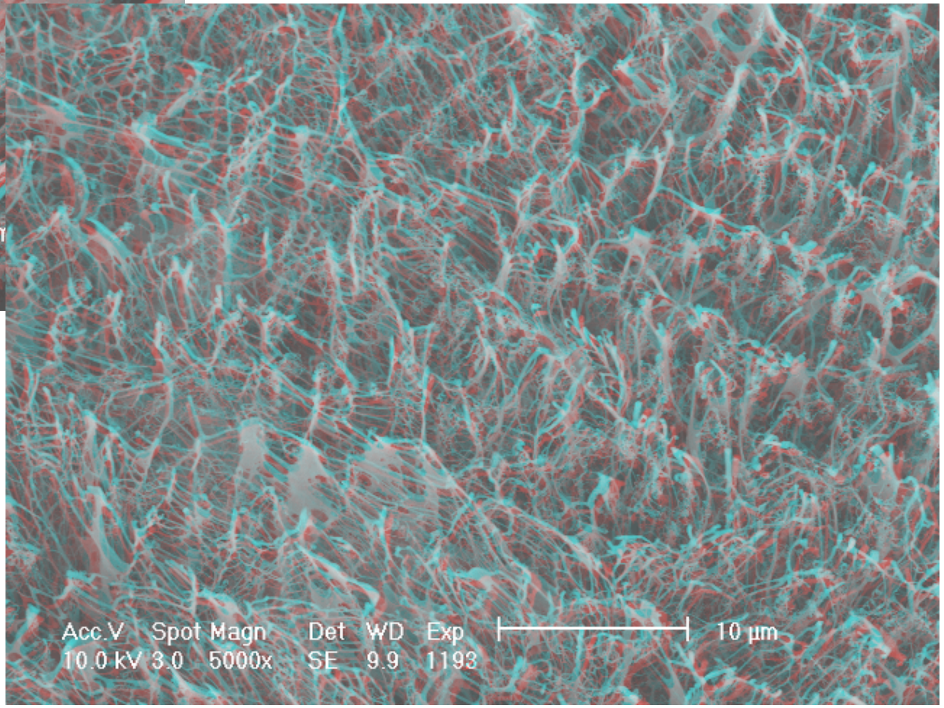
Cryo SEM (105 mM) Liquid



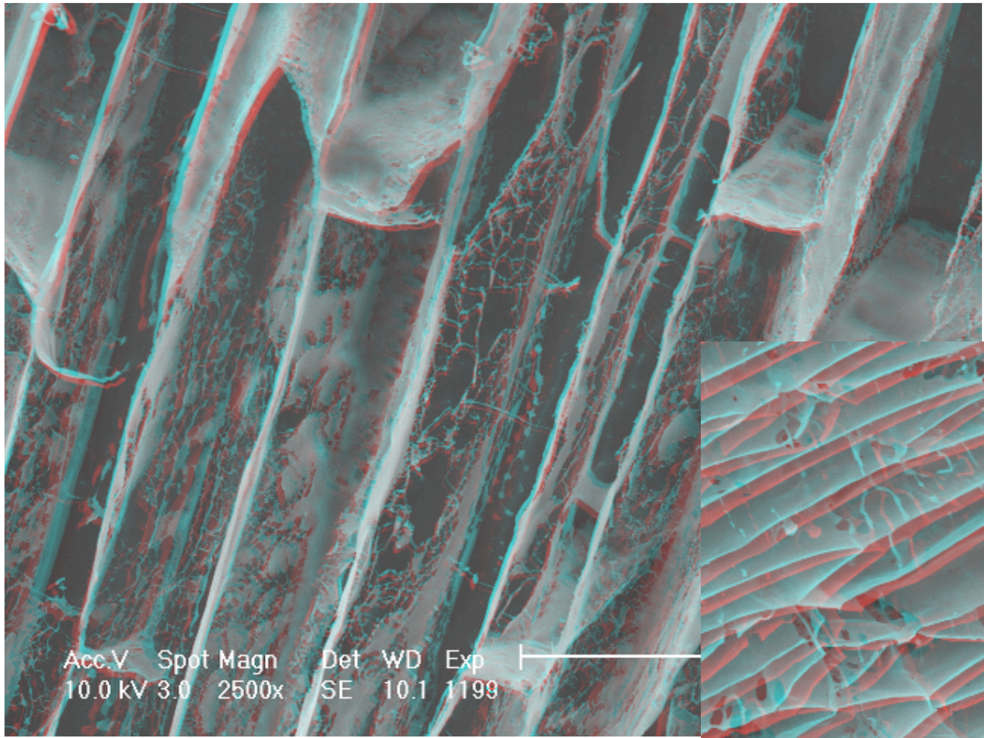


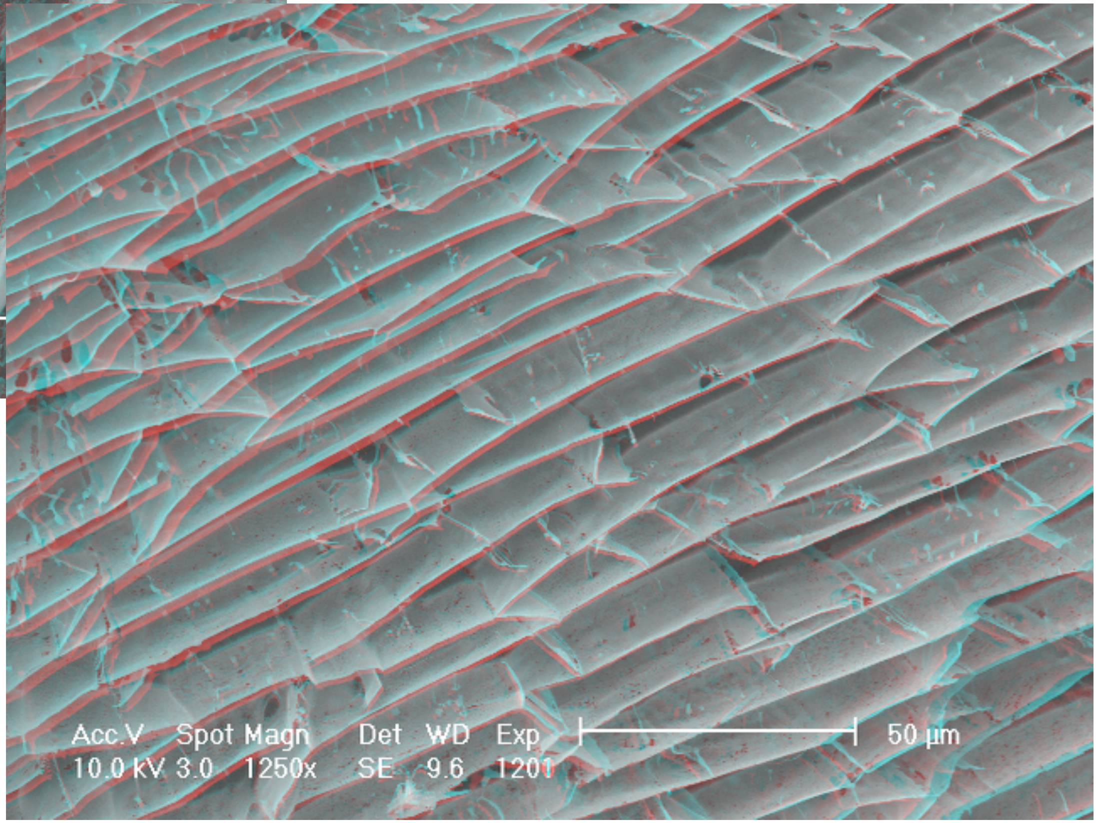
Cryo SEM (1 mM) Gel



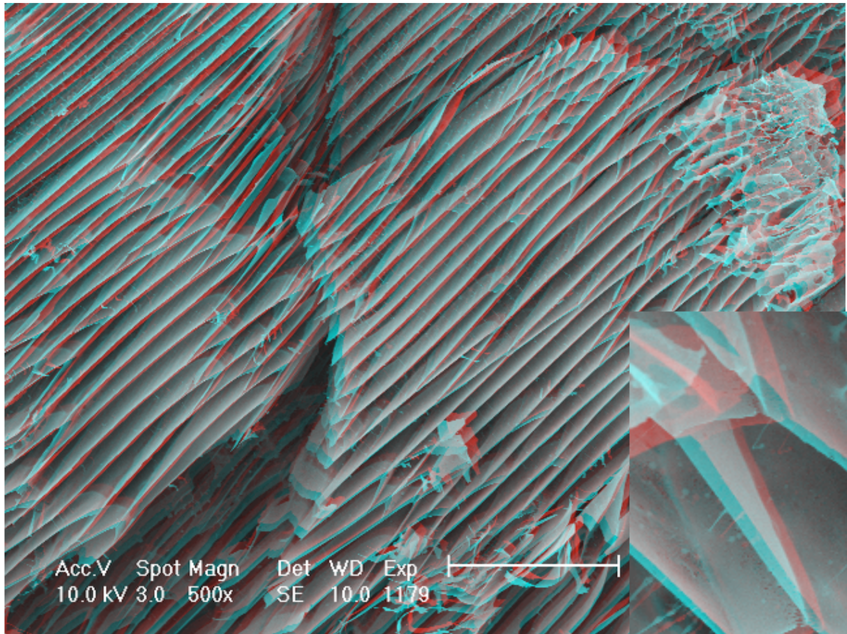


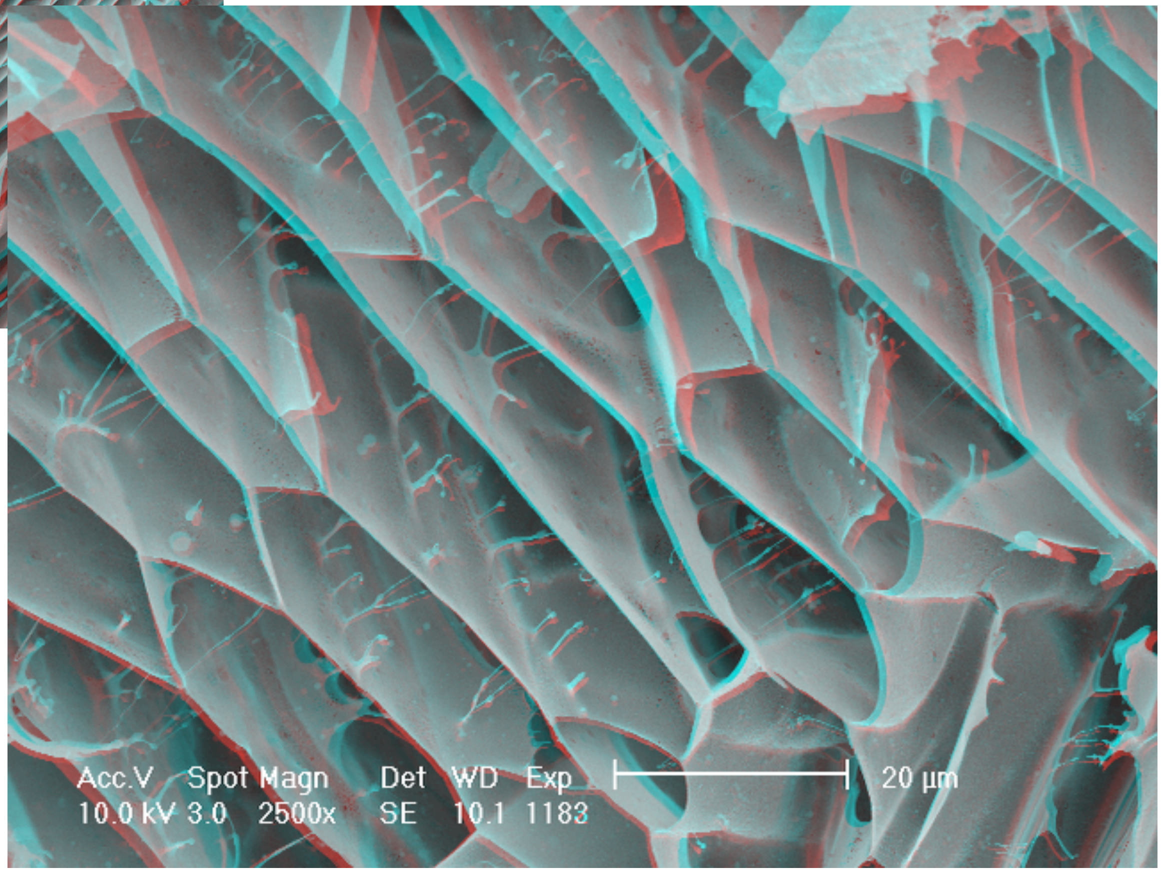
Cryo SEM (105 mM) Gel



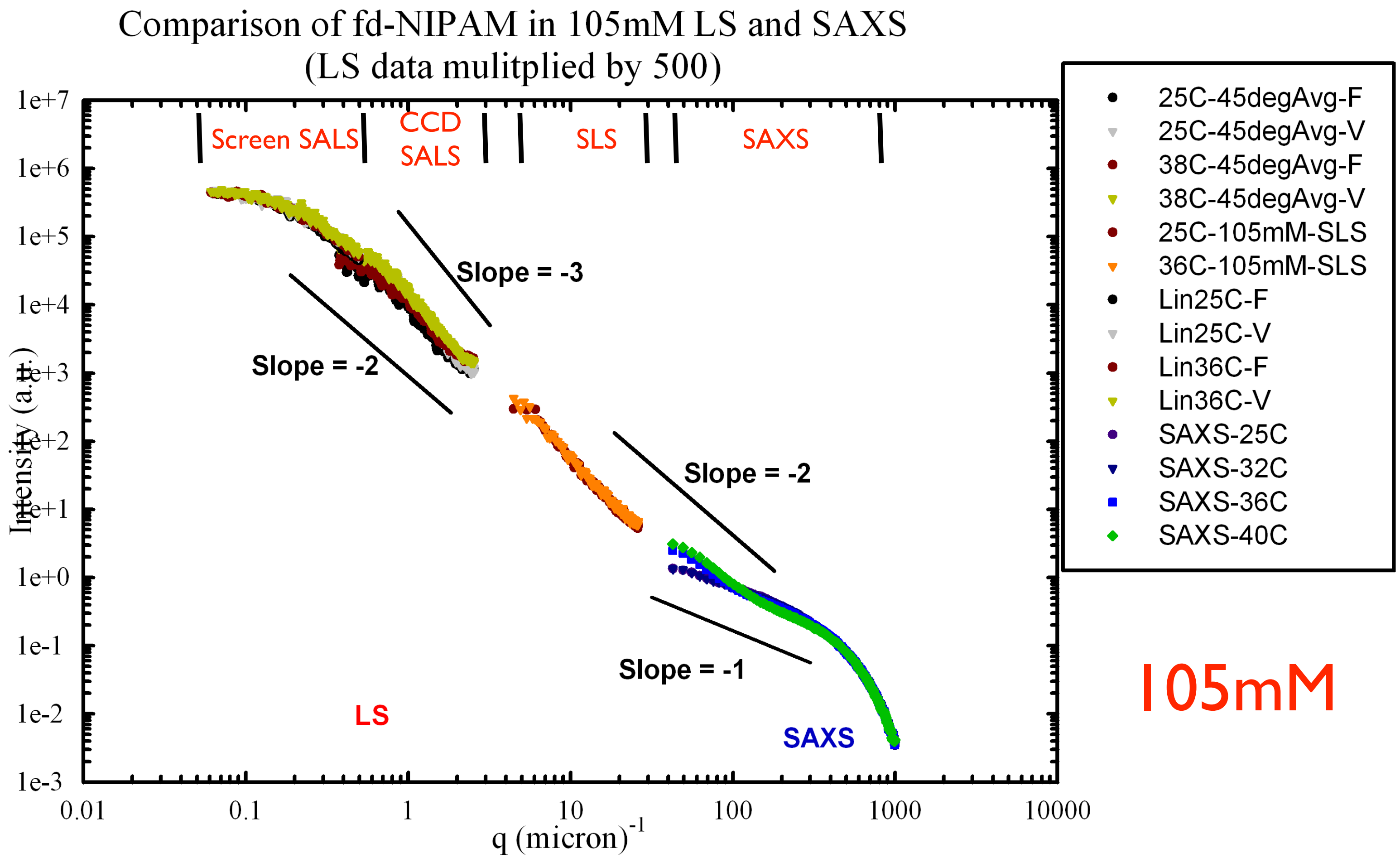


Cryo SEM (Pf1 liquid)





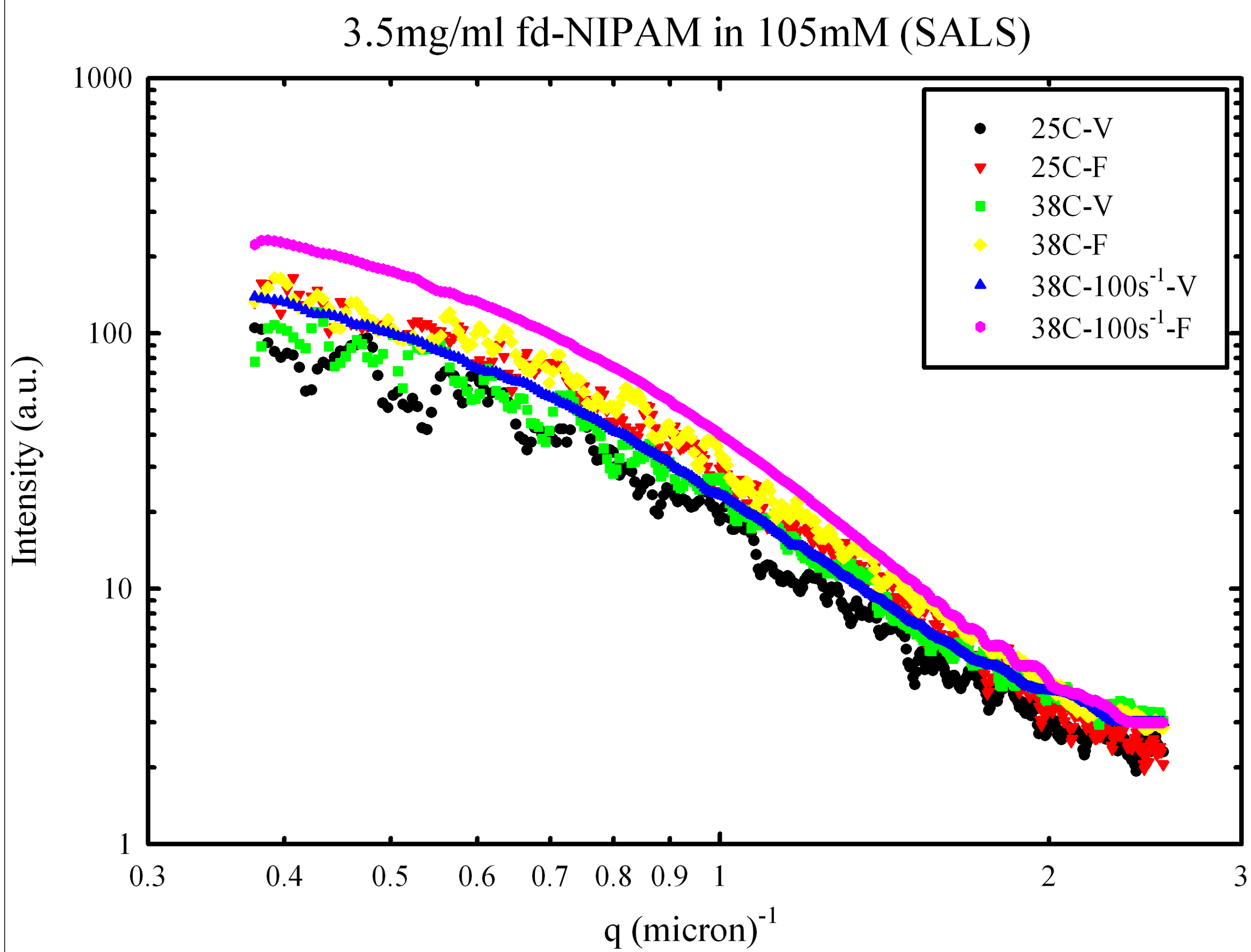
Scattering



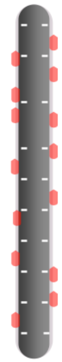
105mM

The above graph is for static conditions
A change from fluid to gel is only seen in SAXS
and a small change in slope at very low q

Scattering shear



105mM



Conclusion

1. Gelation temperature and structure : *Can be varied with ionic strength*
2. Power law scaling seen for *G' and critical strain. They indicate the difference between the two gels (structure and strength). G' scaling agrees with theory, but critical strain scaling is underestimated by the theory (by MacKintosh)*
3. Gel: Unique *S* and *n* values have been obtained
   - *S = f(conc. and ionic strength)* and *n = f(ionic strength)*
4. Cryo-SEM: *shows structural difference between the gels in two ionic strength?*
5. *Scattering techinque*
   1. *Sol to gel transition is seen by SAXS*
   2. *Only shear densification is seen by SALS (a slope of 2 is seen in both sol and gel states and a slope of 3 under shear)*